Deposition of Certain More Active Metals on Copper

A Thesis

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of the requirements for the Degree
of Master of Science in Chemistry

by

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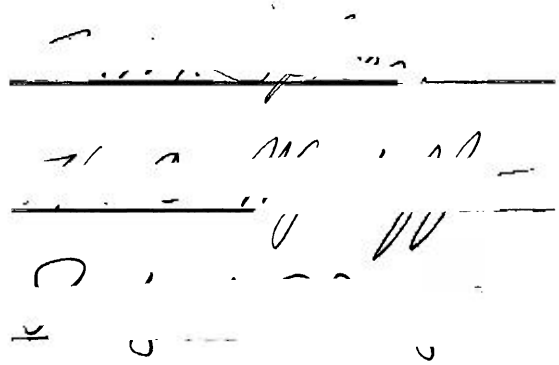

Acknowledgement

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Introduction

In 1873 Raoult (13) reported the fact that a more electro-positive metal could be plated on a less electro-positive metal by purely chemical means. He succeeded in plating cadmium on gold by immersing the two metals while in contact in a solution of a cadmium salt. Unfortunately, Raoult offered no explanation for the mechanism of the process. In 1905 Smith (14) reported the reciprocal replacement of zinc and copper, cadmium and copper, silver and gold, and other metals. Here, as in the case of Raoult, no attempt was made to explain just why the action takes place. However, since the time of these publications, several investigators have attempted to explain this rather unusual phenomenon.

In 1926 two Englishment, Humby and Perrin, (6) reported that when the cell-

zinc,zinc sulfate,copper-

is shorted, zinc, the more electro-positive metal, is deposited on the copper, the less electro-positive metal. No explanation was forthcoming at that time. However, four years later Lottey and Perrin (7) advanced the theory that the action was due to the formation of a porous oxide film of zinc on the copper through which more zinc could diffuse and deposit from the inner surface.

Several patents [Brunskill (1), Burnett (2), Grinlinton

(4), Hull (5), Pacz (8), Pavelish and Sullivan (9), and Pfeil (10)] have been granted on the deposition of certain more active metals on less active metals by purely chemical means. However, as is frequently the case with patents, little useful information could be obtained from any of these. In fact, the author was unable to repeat Burnett's (2) work on the deposition of chromium on iron from a solution in phosphoric acid of chromium or a chromium compound, such as chromite.

In 1937 two Russians, Plotnikov and Zosimovich, (11) measured the potential change of each electrode in the cells- zinc, zinc sulfate, copper and nickel, nickel sulfate, copper- and found that the zinc and nickel potentials did not change. They found also that the zinc potential remained at -0.780 v. during the experiment, but the copper potential changed from 0.22 to -0.700 v. and thus approached the zinc potential. Plotnikov and Zosimovich attributed this change in potential of the copper electrode to the formation of an alloy between the copper and the zinc. Two years later Plotnikov and Zosimovich (12) in another publication advanced the idea that more electro-positive metals deposited on less electro-positive metals because of the change in free energy in the formation of intermediate compounds or solid solutions.

Since no two of the previous investigators could agree on a mechanism for this process, a critical and comprehensive investigation of this problem was undertaken to determine just what metallic couples and electrolytes could be used, and

from the data thus obtained to advance a mechanism which might explain this unusual process.

Materials and Laboratory Procedure

The copper used in this investigation was of the purest electrolytic grade (99.99% copper). Small thin strips about 3/4 inch wide by 2 inches long by 1/32 inch thick were first sand-papered thoroughly to free the surface of any adherent oxide film, washed with either concentrated hydrochloric or moderately strong nitric acid to insure the complete removal of any remaining foreign matter or oxide, washed with distilled water several times, and then rinsed several times with acetone in order to insure the complete removal of any grease which might have been present. (Extreme care was taken not to touch the strip with the hands after it had been cleaned. The copper strip thus prepared was placed in contact with the metal or alloy to be investigated in the desired solution, and the process carried out either at room temperature or by refluxing in an ordinary 500 c.c. round-bottom flask equipped with a water-cooled condenser.

The metals other than copper used in this investigation were in general of the highest technical grade available. However, in the quantitative measurements only chemically pure metals were used.

The solutions used throughout the course of this investigation were prepared from chemically pure grade chemicals with distilled water.

The general laboratory procedure can best be illustrated

by a sample investigation. For example, the procedure for the coating of copper with zinc in a ten per cent sodium hydroxide solution is as follows.

The copper strip is first sand-papered carefully, dipped into concentrated hydrochloric acid, washed several times with distilled water, washed carefully with acetone, kept in a desiccator for at least thirty minutes, weighed, then put in contact with granular zinc in a ten per cent sodium hydroxide solution and the entire contents either heated, or allowed to remain at room temperature until the copper strip appears to be completely coated. After the copper strip is completely coated, it is removed from the solution, washed thoroughly with distilled water to remove the sodium hydroxide and any zinc which may be mechanically held to the surface, dried in a desiccator for at least an hour, and weighed. The difference in the two weighings gives the amount of zinc deposited on the copper, and from this the percentage of zince is calculated.

The usual procedure for the qualitative analysis of the metal ions was followed in the detection of the metals deposited. The coating was first dissolved with a suitable acid (usually concentrated hydrochloric) and this solution analyzed for the metal ions.

The electromotive force of the cells investigated was measured by an ordinary student-type potentiometer.

The results of this investigation are given in tables 1-8 inclusive, and the data of tables 3 and 4, and 5 and 6 are given in graph form on pages 16 and 17 respectively.

Results

Table 1

Tabulation of Metallic Couples Investigated

Metallic Couple	Solution used	Results
1. Al-Cu	10% NaOH	No Reaction
2. Al-Cu	" $AlCl_3$	" "
3. Al-Cu	6N NaOH	" "
4. Al-Cu	Dist. H_2O	" "
5. Al-(Sn on Cu)	10% $CaCl_2$	" "
6. Al-(Sn on Cu)	" $Al_2(SO_4)_3$	" "
7. Cd-Cu	10% NaOH	Cd deposited on Cu
8. Cd-Cu	" H_2SC_4	" " " "
9. Cd-Cu	6N NaOH	" " " "
10. Cd-Cu	Dist. H_2O	Trace of Cd on Cu
11. Cd-Brass	6N NaOH	Cd deposited on Brass
12. Cd-Sn	" "	" " " Sn
13. Co-Cu	10% NaOH	No Reaction
14. Co-Cu	" H_2SO_4	" "
15. Co-Cu	6N NaOH	" "
16. Cr-Cu	10% NaOH	" "
17. Cr-Cu	" H_3PO_4	" "
18. Cr-Cu	6N NaOH	" "
19. Cr-Cu(150° under P*)	" "	" "
20. Cr-Cu	Chrome Alum	" "

*Pressure

Table 1(continued)

Tabulation of Metallic Couples Investigated

Metallic Couple	Solution used	Results
21. Cr-Cu	H_3PO_4,$CuCr_2O_7$	No Reaction
22. Cr-Cu	H_2CrO_4,$CuCl_2$	" "
23. Cr-Pb-Cu	6N NaOH	" "
24. Fe-Cu	10% H_2SO_4	" "
25. Fe-Cu	" H_3PO_4	" "
26. Fe-Cu	" NaOH	" "
27. Fe-Cu	Dist. H_2O	" "
28. Fe-Cu	H_3PO_4,K_2CrO_4,$CuCl_2$	" "
29. Mn-Cu	6N NaOH	Trace of Mn on Cu
30. Mn-Cu	10% H_3PO_4	" " " " "
31. Mn-Cu	Sat. $MnCO_3$	" " " " "
32. Ni-Cu	6N NaOH	No Reaction
33. Ni-Cu	10% H_2SO_4	" "
34. Ni-Cu	10% H_3PO_4	" "
35. Pb-Cu	" NaOH	" "
36. Pb-Cu	6N NaOH	" "
37. Pb-Cu(150° under P)	" "	" "
38. Pb-Cu	10% H_3PO_4	" "
39. Pb-Cu	$Pb(NO_3)_2$,NH_4OH	" "
40. Pb-Cu	" , xs NaOH	" "
41. Pb-Cu	$Pb(OAc)_2$	" "

Table 1(continued)

Tabulation of Metallic Couples Investigated

	Metallic Couple	Solution used	Results
42.	Pb-Cu	H_3PO_4, $PbCr_2O_7$	No Reaction
43.	Pb-Cu	Dist. H_2O	" "
44.	Pb-Ag	$Pb(NO_3)_2$, xs NaOH	" "
45.	Pb-Bi	6N NaOH	Pb deposited on Bi
46.	Sb-Cu	Dist. H_2O	Sb deposited on Cu
47.	Sn-Cu	10% NaOH	Sn " " "
48.	Sn-Cu	6N "	" " " "
49.	Sn-Cu	10% H_2SO_4	" " " "
50.	Sn-Cu	" $KHSO_4$	" " " "
51.	Sn-Cu	" $ZnCl_2$	" " " "
52.	Sn-Cu	Dist. H_2O	" " " "
53.	Sn-Brass	6N NaOH	" " " Brass
54.	Sn-Zn-Cu	" "	Zn " " Cu & Sn
55.	Tl-Cu	" "	No Reaction
56.	Tl-Cu	10% $KHSO_4$	" "
57.	Wood's Metal-Cu	6N NaOH	Sn deposited on Cu Trace of Cd on Cu
58.	Alloy(Pb 87%,Sb)-Cu	" "	No Reaction
59.	Zn-Alloy(Ni 20%,Cu)	" "	Zn deposited on Alloy
60.	Zn-Cu	10% NaOH	Zn deposited on Cu
61.	Zn-Cu(grounded)	" "	" " " "

Table 1(continued)

Tabulation of Metallic Couples Investigated

Metallic Couple	Solution used	Results
62. Zn-Cu	10% H_2SO_4	Zn deposited on Cu
63. Zn-Cu	" $KHSO_4$	" " " "
64. Zn-Cu	" $ZnSO_4$,HCl	" " " "
65. Zn-Cu	" $CaCl_2$	" " " "
66. Zn-Cu	" $SnCl_2$	" " " "
67. Zn-Cu	6N NaOH	" " " "
68. Zn-Cu	$Zn(NH_3)_4SO_4$	" " " "
69. Zn-Cu	Dist. H_2O	" " " "
70. Zn-Cu	C_2H_5OH	No Reaction
71. Zn-Cu	CH_2OH	" "
72. Zn-Cu	CH_2OH CCl_4	" "
73. Zn-Ag	6N NaOH	Zn deposited on Ag
74. Zn-Ag-Cu	10% "	" " " Cu
75. Zn-Bi	" "	No Reaction
76. Zn-Bi	6N "	" "
77. Zn-Brass	" "	Zn deposited on Brass
78. Zn-Graphite	" "	No Reaction
79. Zn-Graphite-Cu	" "	Zn deposited on Cu
80. Zn-Sn	10% NaOH	Trace of Zn on Sn
81. Zn-Sn	6N "	Zn deposited on Sn
82. Zn-Sn	Dist. H_2O	No Reaction
83. Zn-Sn-Cu	6N NaOH	Zn & Sn deposited on Cu
84. Zn-(Sn on Cu)	" "	Zn deposited on strip
85. (Zn & Sn)*-Cu	" "	Zn deposited on Cu Trace of Sn on Cu

*Zn and Sn not in contact with each other but both in contact with Cu.

Table 2

Tabulation of Quantitative Data on Metallic Couples

	Metallic Couple	Solution used	Time of Contact in hours	Percentage Metal deposited
1.	Cd-Cu	10% NaOH	5	0.120
2.	Cd-Cu	" H_2SO_4	5	0.239
3.	Cd-Cu	6N NaOH	8	0.433
4.	Sn-Cu	10% NaOH	100	1.470
5.	Sn-Cu	" H_2SO_4	100	1.410
6.	Sn-Cu	" $KHSO_4$	17	0.598
7.	Sn-Cu	" $ZnCl_2$	5	0.457
8.	Sn-Cu	6N NaOH	23	0.807
9.	Sn-Cu	Dist. H_2O	100	0.380
10.	Zn-Cu	10% NaOH	4	0.369
11.	Zn-Cu	" "	100	14.320
12.	Zn-Cu	" H_2SO_4	1	0.118
13.	Zn-Cu	" $KHSO_4$	11	0.874
14.	Zn-Cu	" $SnCl_2$	5	0.954
15.	Zn-Cu	" $CaCl_2$,HCl	1	0.352
16.	Zn-Cu	" $ZnCl_2$,HCl	8	2.365
17.	Zn-Cu	Dist. H_2O	15	0.140
18.	Zn-(Sn on Cu)	6N NaOH	6	5.840
19.	Zn-Brass	" "	5	0.234
20.	Zn-Ag	" "	15	3.180
21.	Zn-Sn	10% H_2SO_4	5	0.239

Table 3

Tabulation of Percentage Zinc deposited on Copper from a 10% NaOH Solution with respect to Time

Time of Contact in hours	Percentage Zinc deposited
0.17	0.64
0.50	1.03
1	1.53
5	3.33
10	5.22
15	6.74
30	8.91
60	11.59
100	14.26

Table 4

Tabulation of Percentage Zinc deposited on Copper from a 10% H_2SO_4 Solution with respect to Time

Time of Contact in hours	Percentage Zinc deposited
0.17	0.23
0.50	0.39
1	0.51
5	1.78
10	3.36
15	4.53
30	7.29
60	9.03
100	10.55

Table 5

Tabulation of Percentage Tin deposited on Copper from a 10% NaOH Solution with respect to Time

Time of Contact in hours	Percentage Tin deposited
0.17	0.074
0.50	0.148
1	0.295
5	0.662
10	0.882
15	0.954
30	1.062
60	1.385
100	1.470

Table 6

Tabulation of Percentage Tin deposited on Copper from a 10% H_2SO_4 Solution with respect to Time

Time of Contact in hours	Percentage Tin deposited
0.17	---
0.50	0.183
1	0.183
5	0.183
10	0.240
15	0.689
30	1.090
60	1.120
100	1.410

Table 7

Tabulation of the change in E.M.F. for the Cell - Zn,6N NaOH, Zn on Cu* - with respect to time

Time in hours	E.M.F. of Cell	Temperature in °C.
0	0.0150	21
0.5	0.0359	"
1	0.0750	"
2	0.1680	"
7	0.9010	25
22	0.9045	"
26	0.9055	"
40	0.9075	"
192	0.9088	"
204	0.9075	"
228	0.9097	"
230	0.9093	"
236	0.9087	"

E.M.F. for the cell - Zn,6N NaOH,Cu - is approximately 1 v. at 25°C.

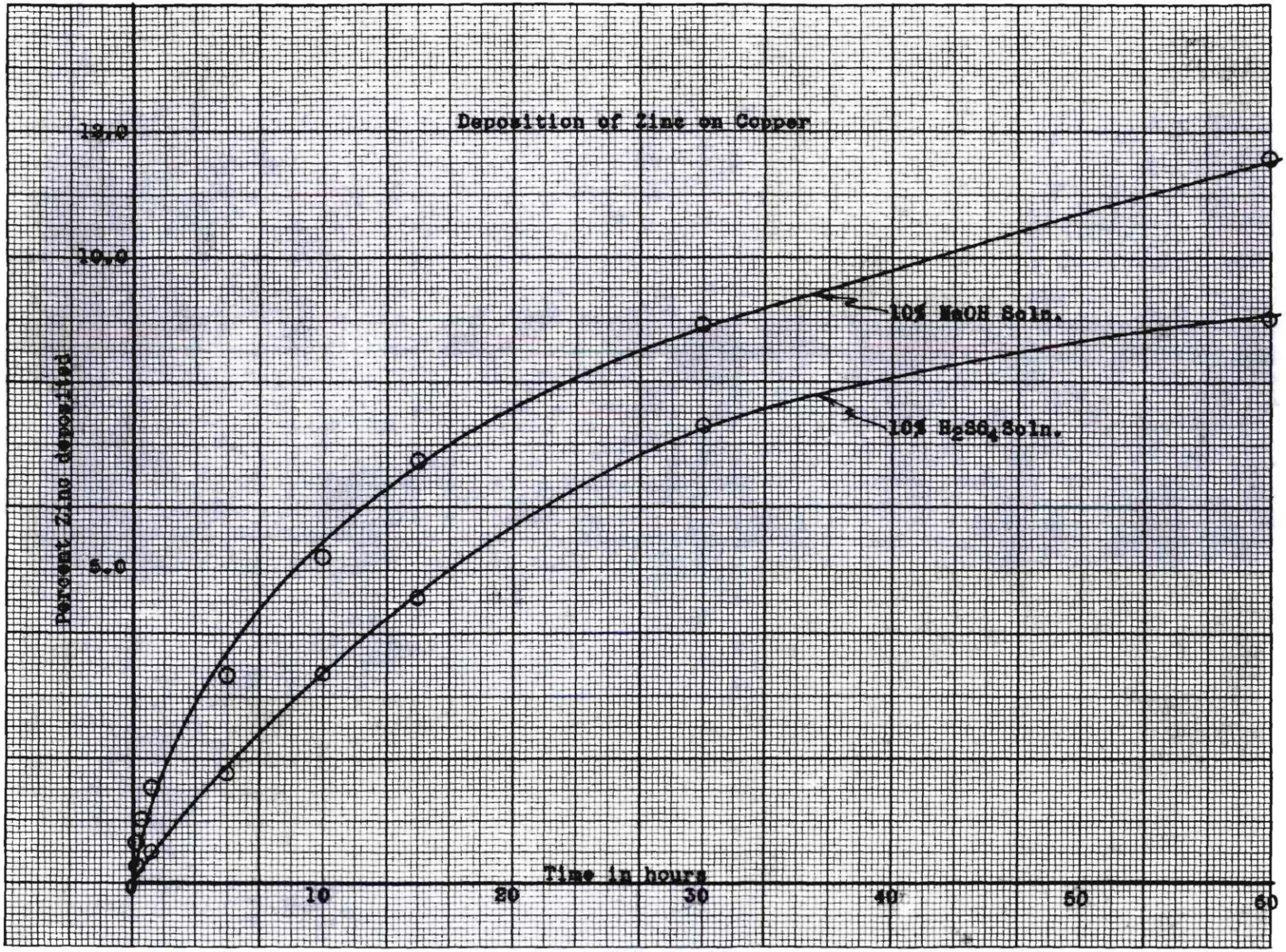
* The copper strip was first coated by being heated in contact with zinc in a 6N sodium hydroxide solution. With the copper strip thus prepared, a cell was set up, and contact made between the two electrodes only at the instant of the E.M.F. readings.

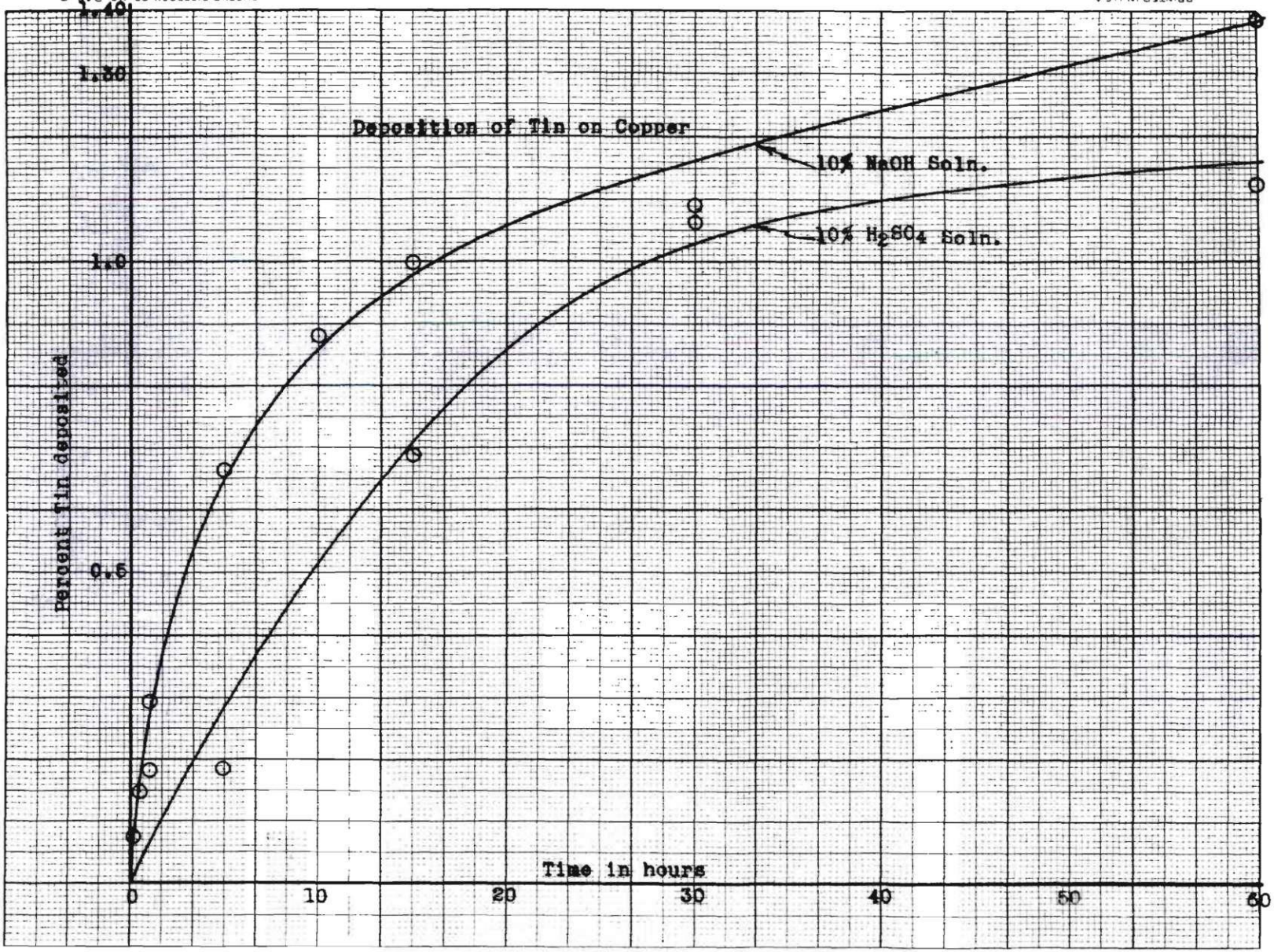
Table 8

Tabulation of change in E.M.F. for the cell- Zn, 6N NaOH, Zn on Ag- with respect to time at 250°C.

Time in hours	E.M.F. of Cell
0	0.0000
2	0.8064
3	1.2073
15	1.2041
23	1.0150
26	1.2025

E.M.F. for the cell- Zn,6N NaOH,Ag- is 1.3065 v. at 250°C




Deposition of Tin on Copper
10% NaOH Soln.
10% H_2SO_4 Soln.
Percent tin deposited
1.40
1.30
1.0
0.6
Time in hours
0
10
20
30
40
50
60

Analysis of Data

From an inspection of table 1, it can be seen that zinc, tin, and cadmium readily plate on copper from either an acid or a basic medium. Under similar conditions aluminum, cobalt, chromium, iron, nickel, lead, and thallium do not plate on copper at all, while only traces of manganese are deposited on the copper. In order to explain these facts one must answer two questions:

1) Why should a highly electro-positive metal like zinc deposit on a less electro-positive metal like copper? This is apparently contrary to what one would expect from a consideration of the activity series of the metals.

2) Why is the reaction specific? Since zinc and tin deposit on copper, why do not all the other metals which lie between these metals in the activity series deposit similarly?

When a small piece of zinc is placed on a large sheet of copper and immersed in a suitable solution, the zinc gradually plates on the copper, starting at the point of contact and gradually spreading away from that point, just as if the zinc were being melted on the copper. Tin and cadmium act in a similar way. These metals have melting points of 419, 232, and 312 degrees respectively. Iron, cobalt, and chromium, which have high melting points, show no tendency to plate in any medium. These facts seemed to indicate that the melting point of the plating metal might be the significant factor. However, lead and thallium, which have melting points of 328

and 304 degrees respectively, do not plate on copper in any medium. Therefore, the idea that the melting point of the plating metal is the significant factor must be rejected.

The possibility of a simple displacement of zinc ions by copper according to the equation,

$$Zn^{++} + Cu \longrightarrow Cu^{++} + Zn,$$

was next considered as a possible mechanism for the process. This mechanism is worth considering in view of the fact that in a solution of a zinc salt the concentration of the zinc ion is high while that of the cupric ion is essentially zero. But there are three experimental reasons for rejecting this mechanism. 1) When sodium hydroxide is used, the concentration of the zinc ion in the solution is very low due to the formation of sodium zincate. 2) If this mechanism were correct, since both tin and zinc plate on copper, any metal between them in the electro-chemical series should also plate; but out of the four metals investigated, (chromium, cobalt, nickel, and cadmium), only cadmium plates on copper. 3) No copper could be found in the solution or on the zinc, a fact which indicated that no metallic copper had dissolved and gone into the form of the cupric ion. Thus, it can be seen that this mechanism does not lend itself to the interpretation of the data obtained in this investigation.

A third possible explanation for this process is based on the fact that certain metals form solid solutions with

each other. When, for example, copper and zinc are heated in contact with each other they form a solid solution. Now, the activity of the zinc in the solid solution is less than that of the pure zinc. Therefore, there is a greater tendency for the pure zinc to form ions than for the zinc from the solid solution. And, since there is an equilibrium existing between both the pure zinc and the solution, and between the zinc of the solid solution and the solution at saturation, it is logical to believe that the pure zinc will deposit on the copper until the activity of the zinc in the solid solution is equal to that of the pure zinc.

The following pairs of metals are known to form solid solutions with each other: 1) cadmium and copper, 2) zinc and copper, 3) tin and copper, 4) manganese and copper, 5) antimony and copper, 6) zinc and silver, and 7) lead and bismuth.

By an inspection of table 1, it can be seen that in each case where the metals are capable of forming solid solutions with each other, the more electro-positive metal deposits on the less electro-positive metal in almost any medium; while with those metals which do not form solid solutions, no action could be obtained under any circumstances. (Very little work was done on the metallic couple, antimony-copper, during the current investigation. However, since antimony forms a solid solution with copper of about 8% antimony, it is suggested that for further work on this problem, this metallic couple be investigated.) Furthermore, when the metals are arranged in

order of the ease with which they coat on a given metal, it is interesting to note that the metal which forms a solid solution of the highest concentration at a low temperature coats more readily and to a greater extent than the metal which forms a solid solution of a lower concentration. This is illustrated well by the fact that zinc, which forms a solid solution with copper of about 30-40% zinc, coats most readily and in the largest amount; while cadmium, which forms a solid solution with copper of only about 2% cadmium, coats with the least ease and in the smallest amount. Tin, which forms a solid solution with copper of about 14% tin, coats more easily and in a larger amount than cadmium, but not as easily and in as large amount as zinc. An inspection of the quantitative data of tables 2, 3, and 4 will verify the above statements. (Above 800 degrees manganese forms a complete series of solid solutions with copper. However, it does not deposit readily on copper at 100 degrees. This would seem to indicate that at lower temperatures manganese shows little tendency to form a solid solution with copper. This is a subject for further investigation.)

A further indication that the action is due primarily to the formation of solid solutions between the metals in question is given by the fact that, lead, which does not form a solid solution with copper, will not deposit on copper in any medium but will deposit on bismuth with which it forms a solid solution; and zinc, which forms a solid solution with silver, will

deposit on silver.

Electromotive force measurements of the cell - Zn,6N NaOH, Cu - after shorting for a definite length of time, indicated that the copper potential was approaching that of the zinc potential. Thus, at the saturation point of the solid solution of zinc and copper an equilibrium is reached between the two electrodes. Or, in other words, the action in the cell is due to the transfer of pure zinc to the copper electrode; and, condequently, at saturation the activity of the zinc in the solid solution being equal to that of the pure zinc, the difference in potential should approach zero. The data in tables 7 and 8 indicate that the surface of the copper electrode is almost completely coated by the zinc. Also, the electromotive force changes more rapidly at first than after a few hours. This fact seems to indicate that some of the zinc has been dissolved in the copper.

An inspection of tables 3, 4, 5 and 6, and of the corresponding graphs of these data on pages 16 and 17 reveals two facts. 1) The deposition of the metal is rapid at first, then decreases gradually in the rate of deposition and appears to approach a maximum. This is attributed to the fact that as more metal is deposited the solid solution approaches saturation at the temperature of investigation. 2) The action takes place more rapidly in a basic than in an acid solution. This is attributed to the fact that zinc reacts with an acid more rapidly than with a base, and, hence, more zinc will be

dissolved per unit time from the coated surface in the acid solution than in the basic solution.

The author believes that the idea of the formation of a porous oxide film of zinc on the copper cathode through which more zinc could diffuse and deposit from the inner surface, advanced by Lottey and Perrin (7), has been discredited by the results of the current investigation. In each case where a more active metal was found to deposit on a less active metal, and especially when zinc was deposited on copper, the coating was found to be quite metallic in appearance. Also, the action takes place just as well in a solution which has been boiled before the immersion of the two metals, and is kept boiling during the coating process. Certainly, there could be little, if any, oxygen in such a solution. Furthermore, the electromotive force measurements indicate that only pure zinc is deposited on the copper electrode.

The results of the current investigation, however, agree well in all instances with the idea that the action is due to the formation of solid solutions.

The following will show why the proposed mechanism of the formation of solid solutions between the metals in question is a sufficient explanation for a driving force for this reaction.

When zinc and copper are brought in contact and immersed in a suitable solution, the zinc, having a higher solution pressure than that of the copper, will become negatively

charged as shown by the following equation:

$$Zn \rightleftharpoons Zn^{++} + 2e.$$

Since there is an equilibrium existing between the metallic zinc and the zinc ions, there is a steady exchange of zinc ions with the solution. Now, since the zinc is in contact with the copper, the copper will acquire the same negative charge as that of the zinc. It is logical to believe that in such a system, some of the zinc ions will be neutralized at the surface of the copper. The zinc ions thus neutralized become metallic zinc and deposit on the copper. Furthermore, the zinc which deposits on the copper will acquire a lower activity than that of the pure zinc, due to the formation of a solid solution, and, consequently, will show less tendency to return to the form of zinc ions. Thus, the zinc coating will build up at the expense of the pure zinc.

When chromium and copper are brought in contact and immersed in a suitable solution, identical equilibria with those of the zinc and copper are set up. However, since chromium does not form a solid solution with copper, the activity of the chromium deposited on the copper will be the same as that of the pure chromium. Consequently, the chromium will dissolve as fast as it is deposited, and, hence, very little, if any, chromium will be deposited on the copper.

Summary and Conclusion

From the current investigation, the following facts are evident:

1) Zinc, tin, cadmium, and manganese can be deposited on copper by purely chemical means at low temperatures.

2) Similarly, zinc can be deposited on silver, and lead can be deposited on bismuth...

3) The action takes place shlowly at room temperature, but rapidly at 100 degrees centigrade.

4) The difference in potential for the cell- Zn,6N NaOH, Cu- approaches zero when the cell is shorted.

From the results of this investigation, the final conclusion is that certain more active metals deposit on less active metals due to the formation of solid solutions between the metals in question.

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